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UNIVERSITY OF CALIFORNIA  
COLLEGE OF AGRICULTURE  
AGRICULTURAL EXPERIMENT STATION  
BERKELEY, CALIFORNIA

# Changes Occurring During Freezing Storage and Thawing of Fruits and Vegetables

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BULLETIN 551

MAY, 1933

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UNIVERSITY OF CALIFORNIA PRINTING OFFICE  
BERKELEY, CALIFORNIA

### ACKNOWLEDGMENTS

The investigations of the rates of temperature changes reported were initiated at the request of and sponsored by the Paperboard Industries Association.

During the course of the above investigations the writers were aided in the temperature measurements by D. J. Tilgner, H. B. Wilcox, and D. S. Glenn. The data on changes in pectin were determined by George Beitzel and Piet Quin; a part of the data on peaches was determined by Walter Richert; and Marcus Sherrill determined some of the data on the inversion of sucrose.

Thanks are due to the Fibreboard Products Company, the Mono Service Company, Inc., the Lily Tulip Paper Cup Company, and the American Can Company for furnishing the containers used in these investigations.

# Changes Occurring During Freezing Storage and Thawing of Fruits and Vegetables<sup>1</sup>

M. A. JOSLYN<sup>2</sup> AND G. L. MARSH<sup>3</sup>

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Owing to the rapidly growing interest in the preservation of fruits and vegetables by freezing storage, investigations have been conducted in the Fruit Products Laboratory, University of California, during the past three years on several important problems encountered in the industry. This report presents the results of preliminary studies upon one of these problems, that of factors affecting the changes during freezing and subsequent thawing.

Description of commercial methods and directions for preparing, packing, and freezing fruits and vegetables are given in Circular 320.

A number of physical, chemical, and bacteriological changes occur during the freezing and subsequent thawing of fruits and vegetables. It is necessary to know the nature of these changes in order to determine what fruits and vegetables can be preserved satisfactorily by freezing and how they should be prepared, packed, frozen, and stored. The changes that occur serve as criteria of the degree of success attained in preserving these products. They also determine the suitability of the product for use by preservers, jelly and jam manufacturers, ice cream manufacturers, and by the housewife.

The physical changes that occur during freezing storage depend chiefly upon ice formation and osmotic action; they involve changes in volume, drained weight, and texture. These physical changes occur principally during freezing and during thawing, but generally not during freezing storage, especially if a constant storage temperature is maintained. The results of studies on rates of temperature change in various products under different conditions are included with physical changes.

The chemical changes that occur during preparation, freezing, and thawing involve changes in composition such as hydrolysis of pectin and sucrose by the hydrolytic enzymes present; changes in color and flavor due to oxidation, largely arising through the activity of oxidizing enzymes; and changes in flavor due to anaerobic respiration and other

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<sup>1</sup> Received for publication July 25, 1932.

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causes. These changes are especially marked during the thawing period, owing to injury to the tissues during freezing.

The variability of much of the material used in these tests due to variety, degree of maturity, and growing conditions, the difficulty of accurately measuring many of the physical and chemical changes which occurred, and the fact that the simple mechanism postulated in some of these tests may not be the one operative in the particular case, introduced certain discrepancies in some of the data presented. Nevertheless the data is valuable for it clearly shows the trend of the results in most cases and in others it indicates the extent to which the factors enumerated above influence the results obtained. Much work has yet to be done before we know in detail the kind of complex changes occurring in fruits and vegetables during freezing storage and thawing and before we can fully apply this knowledge to practice.

#### TEMPERATURE CHANGES DURING FREEZING AND THAWING<sup>4</sup>

If a food product cools too slowly during freezing, it may spoil before it is completely frozen; if it warms too rapidly on thawing, it may spoil during distribution unless rigorous care is taken to insure proper refrigeration. It is necessary, therefore, to know how the size and type of container, the nature of the contents, the type and style of the packing case, and the kind and temperature of the surrounding medium, influence these temperature changes, before definite recommendations can be made for the packing of food to be frozen and for the transportation and distribution of the frozen product.

*Temperature Changes in Sugar Solutions, Sweetened Fruit Juices, and Other Liquids.*—In order to study the effect of the composition and nature of the product on the rate of temperature change during freezing and thawing, determinations were made on the following: water; sugar solutions of various concentrations; sweetened juices, and other liquids; dry pectin; and dry sugar. No. 10 tin cans filled to 90 per cent of their volume were used in these tests. Freezing was at 0° Fahrenheit, in air, and thawing at 70°. Copper-constantan thermocouples sheathed in Bakelite tubes were used to measure the temperature at the center of the containers. The thermocouples were equipped with detachable leads so that connections to the potentiometer could be made through a panel board in the freezing room during cooling and freezing and through another panel board in the thawing room for observation during thaw-

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<sup>4</sup> Some of the results reported here have appeared in other publications. See reference numbers 7, 9, and 10 listed in the terminal bibliography. References 9 and 10 were published subsequent to the date when this manuscript was first submitted for publication.

ing and warming. The temperature data recorded were either checked with those of a preliminary experiment, or by duplicate determinations made at the same time. The results for sugar solutions, which are typical of the other products, are shown in figures 1 and 2. The rate of tempera-

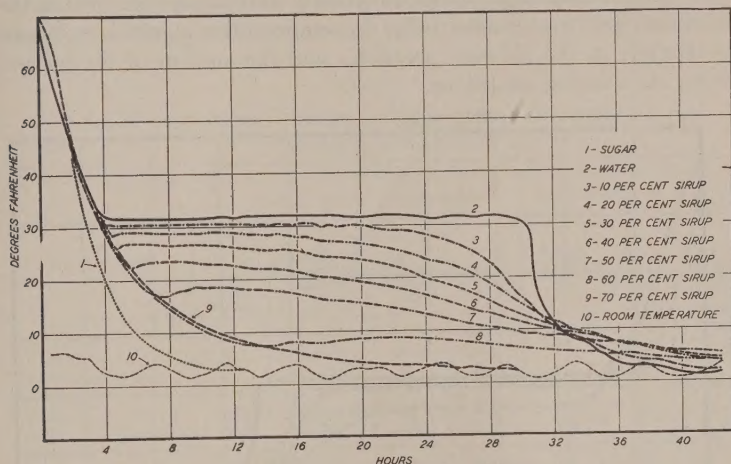


Fig. 1.—Temperature changes in No. 10 cans of water, cane sugar, and sirups during freezing.

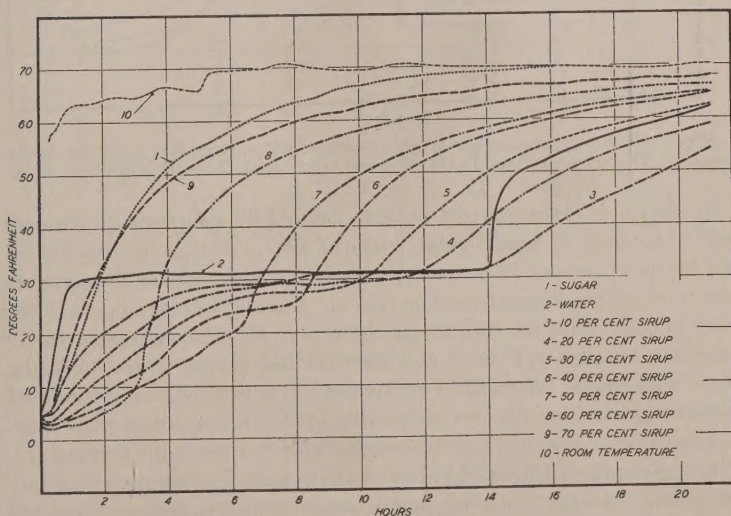


Fig. 2.—Temperature changes in No. 10 cans of water, cane sugar, and sirups during thawing.



ture change increased with increase in sugar concentration but was not appreciably affected by changes in viscosity. The rate of temperature change was not directly proportional to the sugar concentration. The chief factors that determined the rate of temperature change under the conditions of these experiments apparently were the specific heat of the solutions, their heat conductivity, the temperatures at which ice began to separate in the different solutions, and the amount of ice formed under the freezing conditions.

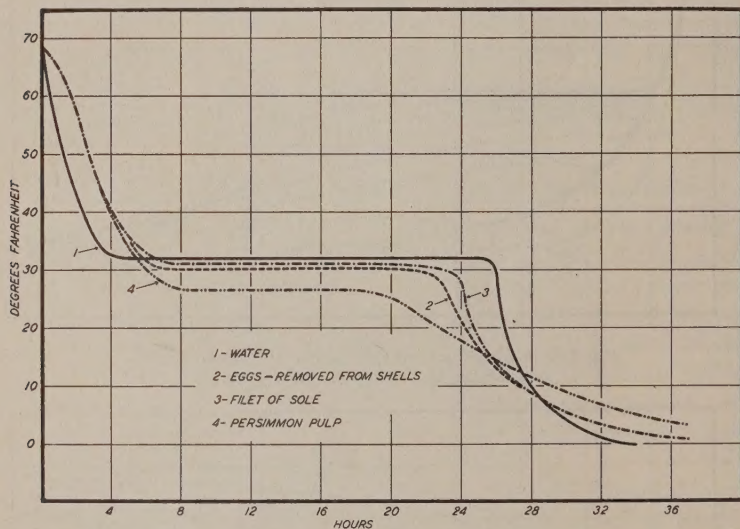


Fig. 3.—Temperature changes in No. 10 cans of water, eggs, fish, and fruit during freezing. The curves for the latter products are typical for solid and pasty foods.

In figure 1, three distinct periods defined by temperature changes will be noted. This is particularly true of water. During the first period the center of the can falls in temperature fairly rapidly as the contents lose their heat to the surrounding cold air. During the second period, the zone of maximum ice formation, the center of the can is at a fairly constant temperature since the material has cooled to its "freezing zone" and heat is liberated by change of water to ice. During the third period representing the further cooling of the frozen product, the temperature of the contents approaches the temperature of the refrigerant.

Sugar solutions differed from water in the following respects. The rate of cooling increased with increase of sugar concentration; the freezing zone was lower, the higher the concentration of sugar; the period of

fairly constant temperature was shorter, the higher the concentration of sugar; and the cooling of frozen sirup was slower than that of ice.

*Temperature Changes in Various Food Products.*—To determine how the rates of temperature change in pasty, semisolid, and solid products differ from those of sugar solutions, the temperature changes in certain meats, fish, vegetable and fruit products were determined by

TABLE 1  
RATES OF TEMPERATURE CHANGES IN VARIOUS BERRY PRODUCTS DURING  
FREEZING AND THAWING

| Berry product             | Freezing period at 2° Fahrenheit         |  |                            |                               | Thawing period at 68° Fahr. |                             |                                |
|---------------------------|--|--|----------------------------|-------------------------------|-----------------------------|-----------------------------|--------------------------------|
|                           | Hours to reach approximate freezing zone | Approximate freezing zone, degrees Fahr. | Hours during freezing zone | Total hours to reach 5° Fahr. | Hours to reach 25° Fahr.    | Hours from 25° to 31° Fahr. | Total hours to reach 65° Fahr. |
| Blackberries:             |  |  |                            |                               |                             |                             |                                |
| Plain.....                | 7½                                       | 28. 4-29. 0                              | 13½                        | 33                            | 7½                          | 5¾                          | 22                             |
| In 40 per cent sirup..... | 7½                                       | 25. 2-26. 0                              | 14                         | 41                            | 9                           | 1¾                          | 24                             |
| Loganberries:             |  |  |                            |                               |                             |                             |                                |
| Plain.....                | 8¾                                       | 29. 2-29. 9                              | 16¼                        | 33¾                           | 6½                          | 7¾                          | 23                             |
| In 40 per cent sirup..... | 8¾                                       | 24. 4-25. 5                              | 12¾                        | 38½                           | 6½                          | 3                           | 23                             |
| Raspberries:              |  |  |                            |                               |                             |                             |                                |
| Plain.....                | 7¾                                       | 29. 6-30. 8                              | 17¼                        | 33                            | 5¼                          | 6¼                          | 24                             |
| In 40 per cent sirup..... | 8½                                       | 28. 0-28. 2                              | 12                         | 40                            | 8¾                          | 2½                          | 24                             |
| Strawberries:             |  |  |                            |                               |                             |                             |                                |
| With sugar, 2 : 1.....    | 7½                                       | 25. 2-26. 2                              | 8                          | 33½                           | 8¾                          | 2½                          | 22                             |
| With sugar, 3 : 1.....    | 7  | 26. 7-27. 2                              | 7                          | 35½                           | 9¼                          | 1¾                          | 22½                            |
| With sugar, 4 : 1.....    | 7  | 27. 2-27. 8                              | 7                          | 39                            | 10                          | 1                           | 23½                            |
| With sugar, 5 : 1.....    | 7½                                       | 27. 3-27. 8                              | 11½                        | 36½                           | 9¼                          | 1¼                          | 23                             |
| In water.....             | 10½                                      | 30. 2-30. 8                              | 17½                        | 37¾                           | 4                           | 13                          | 30                             |
| In 20 per cent sirup..... | 9½                                       | 29. 2-29. 8                              | 13½                        | 39½                           | 6                           | 9¼                          | 27                             |
| In 40 per cent sirup..... | 8½                                       | 27. 8-28. 4                              | 13½                        | 40½                           | 9                           | 4                           | 26                             |
| In 50 per cent sirup..... | 9  | 27. 7-28. 0                              | 11                         | 40½                           | 9                           | 3¾                          | 24                             |
| In 60 per cent sirup..... | 9  | 27. 8-28. 0                              | 8½                         | 37½                           | 9½                          | 2½                          | 23                             |
| In 70 per cent sirup..... | 8  | 27. 3-27. 7                              | 10                         | 34½                           | 8¾                          | 3                           | 24                             |
| Crushed.....              | 7½                                       | 29. 7-30. 1                              | 17                         | 37¾                           | 5¾                          | 11½                         | 27                             |
| Sugar, dry.....           | .....                                    | .....                                    | .....                      | 7                             | 2                           | ¾                           | 9½                             |
| Water.....                | 4½                                       | 32                                       | 27                         | 36¾                           | ¾                           | 12½*                        | 25                             |

\* This period in the case of water was from 25° to 33° Fahrenheit.

the method described in the foregoing section. Results typical of the various classes of products are shown in figure 3. In general, the rate and nature of temperature changes were found to be similar to those in sugar solutions. The solid and semisolid products cooled more slowly to the freezing zone, and below, than did water. Where the separation of much ice occurred, the products thawed more slowly than did water. Products such as peas in brine and Royal Anne cherries in sirup did not differ appreciably in behavior from pasty products, such as prune pulp.



*Temperature Changes in Berries Packed with Sugar or Sirup*—Berries are commonly frozen either with added sugar or in sirup. Therefore, in order to determine how the proportion of fruit to sugar or the concentration of sirup used affects the rate of heat transfer, tests were made as in the preceding section. The data obtained are summarized in table 1. No very marked differences were found in the rates of temperature change of the various berries in 40° Balling sirup. This confirms the work of Diehl *et al.*<sup>(3)</sup> who report that "there appears to be little significant difference in the rate of cooling of strawberries, raspberries, or logan or other berries."

The rates of temperature change increased somewhat with increase in the proportion of sugar to fruit and with the concentration of sirup used. The increase in rate of temperature change with increase of concentration of sirup in the presence of berries was not as great as for the sugar solutions that did not contain berries.

Diehl *et al.*<sup>(3)</sup> also found that the fruit packed with cane sugar cooled slightly faster than fruit packed without sugar; and the more sugar in the pack, the more rapid was the rate of cooling. Barrels of berries were used in Diehl's experiments and therefore the degree of the effect observed was greater than with the smaller containers used in our tests.

In order to determine how the change in texture and sugar absorption resulting from the freezing and thawing affects the rate of heat transfer, the berries used above were refrozen and thawed. It was found that there was a slight increase in the rate of heat transfer, owing probably to increase in sugar content of the berries and to increase in surface exposed per unit volume, brought about by shrinkage. The most noticeable change was the spreading between the curves of the individual series.

#### EFFECT OF TREATMENT ON TEMPERATURE CHANGES IN SEVERAL VARIETIES OF VEGETABLES

In order to determine how the kind of vegetable and methods of pre-treatment affect the rates of temperature change, the temperature changes in asparagus, peas, string beans, and spinach were determined as before. The results obtained are summarized in table 2.

It was found that the freezing zone, during which the temperature remained sensibly constant, was lower in the products having lower moisture content. The rate of cooling, however, increased as the moisture content decreased. The differences in the rate of temperature change observed in unblanched vegetables packed in 5 per cent brine, and in



the ground vegetables were due in part to differences in ingoing weights, arising as a result of filling the cans to 90 per cent of their capacity by volume.

Blanching the asparagus had but little effect on the rate of temperature change, whether packed without liquid, plain, or in brine. This was

TABLE 2  
RATES OF TEMPERATURE CHANGES IN VARIOUS VEGETABLE PRODUCTS DURING  
FREEZING AND THAWING

| Vegetables             | Freezing period at 2° Fahrenheit         |  |                            |                               | Thawing period at 68° Fahr. |                             |                                |
|------------------------|--|--|----------------------------|-------------------------------|-----------------------------|-----------------------------|--------------------------------|
|                        | Hours to reach approximate freezing zone | Approximate freezing zone, degrees Fahr. | Hours during freezing zone | Total hours to reach 5° Fahr. | Hours to reach 29° Fahr.    | Hours from 29° to 31° Fahr. | Total hours to reach 65° Fahr. |
| Hulled peas:           |  |  |                            |                               |                             |                             |                                |
| Ground.....            | 7  | 29.3-30.0                                | 12                         | 27½                           | 12¾                         | ½                           | 26                             |
| Plain.....             | 8½                                       | 29.3-29.8                                | 8                          | 28                            | 11                          | 2½                          | 24½                            |
| In brine.....          | 8  | 29.6-30.0                                | 7                          | 33                            | 12½                         | 1                           | 29½*                           |
| Cut string beans:      |  |  |                            |                               |                             |                             |                                |
| Ground.....            | 8¼                                       | 30.8-30.9                                | 15½                        | 32                            | 10                          | 6                           | 29½*                           |
| Plain.....             | 8¼                                       | 29.8-30.3                                | 8¼                         | 25½                           | 9                           | 3¾                          | 24½                            |
| Plain in brine.....    | 6¼                                       | 29.8-30.2                                | 8¼                         | 33½                           | 12¾                         | 1½                          | 29½*                           |
| Blanched.....          | 7  | 30.3-30.7                                | 8                          | 24½                           | 6¼                          | 4¾                          | 23½                            |
| Blanched in brine..... | 6¼                                       | 29.9-30.3                                | 10¼                        | 33½                           | 12¾                         | 2                           | 29½*                           |
| Spinach:               |  |  |                            |                               |                             |                             |                                |
| Ground.....            | 8½                                       | 30.2-30.3                                | 12½                        | 29½                           | 12                          | 2¼                          | 29½*                           |
| Plain.....             | 8½                                       | 29.5-30.2                                | 5¾                         | 22                            | 7                           | 1½                          | 18                             |
| Plain in brine.....    | 7¾                                       | 29.3-30.3                                | 9¼                         | 30½                           | 11                          | 1¾                          | 24½                            |
| Blanched.....          | 7  | 30.3-30.8                                | 13½                        | 29½                           | 12¾                         | 1¾                          | 28                             |
| Blanched in brine..... | 7  | 30.3-30.7                                | 11                         | 33                            | 11¼                         | 1                           | 28                             |
| Asparagus stalks:      |  |  |                            |                               |                             |                             |                                |
| Ground.....            | 8½                                       | 31.1-31.2                                | 15                         | 32                            | 9¼                          | 6                           | 29½*                           |
| Plain.....             | 8¼                                       | 30.4-30.7                                | 12                         | 29½                           | 8½                          | 7½                          | 28                             |
| Plain in brine.....    | 8¼                                       | 30.5-30.7                                | 12¼                        | 35                            | 13½                         | 2½                          | 29½*                           |
| Blanched.....          | 8½                                       | 31.0-31.1                                | 9                          | 28½                           | 10½                         | 9                           | 29½*                           |
| Blanched in brine..... | 7¼                                       | 30.6-31.0                                | 16¼                        | 34                            | 12¾                         | 4¼                          | 29½*                           |

\* After 29½ hours, at the conclusion of the experiment, these samples had not reached 65° Fahrenheit.

also true of string beans. The blanching of spinach had a marked effect because it wilted the leaves so that more than twice the weight of blanched spinach could be packed in the volume occupied by the raw spinach.

*Effect of Type, Size, and Shape of Container on Rate of Temperature Change.*—The rate of heat transfer, especially where it is limited to conduction, depends to a large extent on the size and shape of the container. In containers of equal capacity, the greater the surface exposed to the refrigerating medium, the more rapid is the cooling. The rate of heat transfer in 40 per cent sirup in tin cans of various sizes was found to

be not directly proportional to the surface exposed per unit volume of contents, but increased progressively with increase in the size of the container and with increase in surface exposed per unit volume. The extent of the difference in rate of temperature change between containers of various size and kind is shown in table 3.

TABLE 3  
RATES OF TEMPERATURE CHANGES IN 40 PER CENT SIRUP IN TIN, PAPER,  
AND GLASS CONTAINERS OF VARIOUS SIZES

| Container                        | Freezing period          |                             |                         | Thawing period           |                             |                          |
|----------------------------------|--------------------------|-----------------------------|-------------------------|--------------------------|-----------------------------|--------------------------|
|                                  | Hours to reach 31° Fahr. | Hours from 31° to 25° Fahr. | Hours to reach 5° Fahr. | Hours to reach 25° Fahr. | Hours from 25° to 31° Fahr. | Hours to reach 65° Fahr. |
| 4-ounce can.....                 | ¾                        | ¾                           | 6                       | 1¼                       | ½                           | 6                        |
| 8-ounce can.....                 | 1¼                       | ¾                           | 8½                      | 2                        | ¾                           | 6½                       |
| 6-ounce flat can.....            | 1¼                       | ¾                           | 7¾                      | 2                        | ½                           | 6½                       |
| No. 1 Eastern oyster can.....    | 1¼                       | ¾                           | 8½                      | 2                        | ½                           | 6½                       |
| No. 1 tall can.....              | 1½                       | ¾                           | 11½                     | 2¾                       | ½                           | 8½                       |
| No. 2 tall can.....              | 1½                       | ½                           | 13                      | 2¾                       | ¾                           | 9½                       |
| No. 2½ can.....                  | 1¾                       | ½                           | 15                      | 3¾                       | 1                           | 12                       |
| 1-pound flat can.....            | 1¾                       | ¾                           | 12                      | 2½                       | ½                           | 8½                       |
| No. 10 Sanitary can.....         | 3½                       | 1                           | 31                      | 8                        | 1                           | 24                       |
| No. 10 friction-top can.....     | 3¾                       | 1¼                          | 30                      | 7½                       | 1¼                          | 23½                      |
| 10-pound friction-top can.....   | 4¼                       | 1½                          | 40                      | 10½                      | 1½                          | 28½                      |
| 15-pound friction-top can.....   | 4¾                       | 1½                          | 45                      | 9½                       | 2½                          | 30                       |
| 30-pound friction-top can.....   | 7                        | 2                           | 65                      | 15                       | 4½                          | 47                       |
| 5-gallon can.....                | 5¾                       | 1½                          | 61                      | 16                       | 5½                          | 46                       |
| 4-ounce Mono tub.....            | ¾                        | ¾                           | 6½                      | 1                        | ½                           | 6                        |
| 8-ounce Mono tub.....            | 1                        | ¾                           | 7¾                      | 1½                       | ¾                           | 7                        |
| 16-ounce Mono tub.....           | 1                        | ¾                           | 10½                     | 2¼                       | ½                           | 9½                       |
| 32-ounce Mono tub.....           | 2                        | ¾                           | 13½                     | 3¾                       | 1½                          | 13                       |
| 16-ounce Tulip Nestrite cup..... | 1¼                       | ½                           | 10½                     | 2¾                       | ½                           | 9                        |
| 32-ounce Tulip Nestrite cup..... | 1¾                       | ¾                           | 13                      | 2¾                       | 1                           | 12¾                      |
| 8-ounce Purity P. B.....         | 1¼                       | ¾                           | 5                       | 1¾                       | 1                           | 8                        |
| 16-ounce Purity P. B.....        | 1½                       | ½                           | 11½                     | 3                        | ¾                           | 10½                      |
| 32-ounce Purity P. B.....        | 2                        | ¾                           | 14                      | 3¾                       | ¾                           | 15                       |
| 64-ounce Purity P. B.....        | 2¾                       | 1                           | 20                      | 5½                       | ½                           | 19                       |
| 4-ounce glass bottle.....        | ¾                        | ¾                           | 6¼                      | 1¼                       | ½                           | 5                        |
| 8-ounce glass bottle.....        | 1                        | ¾                           | 8                       | 1¾                       | ¾                           | 7                        |
| 12-ounce glass bottle.....       | 1¼                       | ½                           | 9                       | 2¼                       | ¾                           | 7                        |
| 32-ounce glass bottle.....       | 1¾                       | ½                           | 12½                     | 3½                       | ¾                           | 10½                      |
| 16-ounce Mason jar.....          | 1¼                       | ½                           | 9¼                      | 2¾                       | ¾                           | 7½                       |
| 32-ounce Mason jar.....          | 1¾                       | ½                           | 12                      | 3½                       | ¾                           | 10                       |
| 1-gallon jug.....                | 3¼                       | 1¾                          | 28½                     | 8                        | 1¾                          | 22                       |
| 5-gallon jug.....                | 5¾                       | 1¾                          | 63                      | 17                       | 3                           | 45                       |
| 4-ounce milk bottle.....         | 1                        | ¾                           | 6¼                      | 1¼                       | ¾                           | 4½                       |

The rates of temperature change in various paper and glass containers decreased progressively as the size of the container increased. It was impossible, however, in this experiment to show whether the size, shape, or the material from which the container was constructed was the most important in determining the rate of temperature change. It was

found that the rates of cooling and warming in the pint cylindrical Purity Paper Bottles, the pint, tall Nestrite cup, the squat 16-ounce Kleen Kup and the 16-ounce flat tin can used by the industry for freezing storage of fruits did not vary materially from each other. Because the small containers were of different shapes, and of different wall thickness, the effect of the materials of construction such as paper, glass, and tin could not be determined accurately. However, it appeared that there was little difference in the rates of cooling and thawing of products in containers of similar size and shape.

*Effect of Initial Temperature.*—To determine the effect of the initial temperature on the rate of cooling, water, 40 per cent sirup, and prune pulp packed in No. 10 cans were brought to various initial temperatures

TABLE 4

EFFECT OF INITIAL TEMPERATURE ON RATE OF TEMPERATURE CHANGE IN WATER, SIRUP, AND PRUNE PULP DURING FREEZING

| Product                 | Initial temperature, degrees Fahr. | Hours to reach freezing zone * | Freezing zone, degrees Fahr. | Hours during freezing zone | Hours to reach 0° Fahr. |
|-------------------------|------------------------------------|--------------------------------|------------------------------|----------------------------|-------------------------|
| Water.....              | 179.0                              | 8½                             | 32                           | 18½                        | 30                      |
|                         | 139.3                              | 8                              | 32                           | 19                         | 29½                     |
|                         | 110.6                              | 7½                             | 32                           | 19                         | 28¾                     |
|                         | 73.1                               | 4¾                             | 32                           | 18¾                        | 26½                     |
|                         | 54.8                               | 3¼                             | 32                           | 19                         | 26¼                     |
|                         | 39.2                               | 1¾                             | 32                           | 20                         | 25¾                     |
| Sirup, 40 per cent..... | 181.3                              | 10                             | 16.0-16.3                    | 4½                         | 29                      |
|                         | 139.7                              | 9½                             | 18.5-20.0                    | 7                          | 29¾                     |
|                         | 112.6                              | 8                              | 18.7-21.0                    | 9½                         | 28¾                     |
|                         | 73.1                               | 6½                             | 18.7-21.2                    | 12½                        | 29                      |
|                         | 56.1                               | 5½                             | 18.7-21.2                    | 12½                        | 28                      |
|                         | 40.2                               | 4¾                             | 18.8-21.2                    | 10                         | 23¾                     |
| Prune pulp.....         | 161.9                              | 16                             | 15.7-16.3                    | 4                          | 31½                     |
|                         | 134.3                              | 14                             | 15.7-16.3                    | 6                          | 28¾                     |
|                         | 106.5                              | 12                             | 15.7-16.3                    | 7                          | 28                      |
|                         | 73.7                               | 11                             | 15.7-16.3                    | 7½                         | 30½                     |
|                         | 53.6                               | 9                              | 15.7-16.3                    | 7½                         | 26¾                     |
|                         | 34.1                               | 7½                             | 15.7-16.3                    | 5½                         | 27½                     |

and transferred to the freezing room where cooling and freezing rates were determined. The data presented in table 4 indicate the extent to which increasing the initial temperature increases the time necessary to reach the freezing temperature. This effect is most marked for water.

*Effect of Low-Temperature Freezing.*—The rates of temperature change in a number of products during freezing at 2° F in air, and at -110° F in solid carbon dioxide, were determined. Typical results are



shown in figure 4. The rate of freezing in solid carbon dioxide was about five times as fast as in air at  $2^{\circ}$ ; cooling to  $30^{\circ}$  F in solid carbon dioxide required from one-half to one hour, depending upon the nature of the product. In general, the products frozen at  $-110^{\circ}$  F cooled more rapidly to the freezing point, had a lower apparent freezing point, and a much shorter freezing period than those frozen at  $2^{\circ}$  F. During thawing

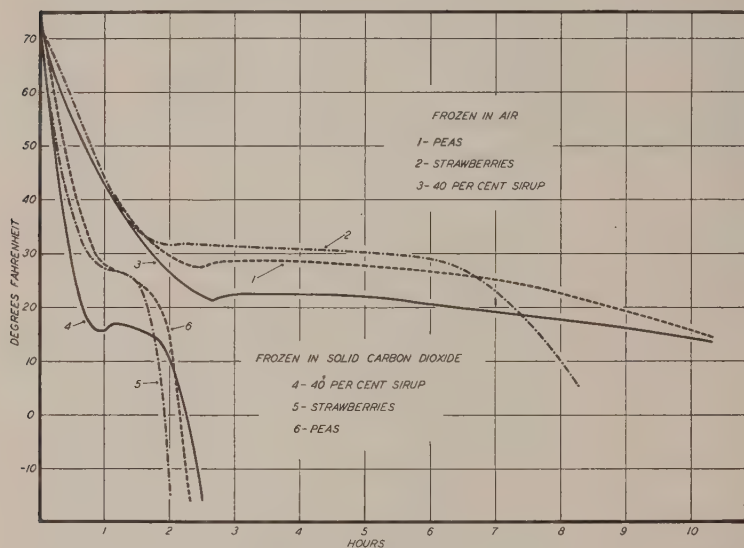


Fig. 4.—Temperature changes in peas and strawberries packed in paraffined paper cartons and in sirup packed in one-pound flat tin cans during freezing in air at  $2^{\circ}$  F and in solid carbon dioxide at  $-110^{\circ}$  F.

the products frozen at  $2^{\circ}$  F in air warmed appreciably faster than those first frozen at  $-110^{\circ}$  F in solid carbon dioxide and then brought to  $2^{\circ}$  F for comparison. The water and the sirup were packed in 16-ounce flat tin cans; the meat, berries, and vegetables in 1-pound folding paper cartons; the corn and whole peaches were directly exposed to the refrigerant.

*Investigations of Temperature Changes in Various Fibreboard Cases.*<sup>5</sup>—Temperature changes in the various small containers used

<sup>5</sup> Fibreboard cases are of two general types. The R. S. C. or regular slotted case is cut out so that only the two side flaps meet at the center while the end flaps which they overlap do not meet in the center. The C. S. S. C. or center special slotted case is cut out so that the two end flaps as well as the two side flaps meet at the center when folded over in closing. The cases are constructed either of solid fibreboard or of corrugated fibreboard.

commercially—the 16-ounce flat tin cans, the various paraffined paper cups and the folding cartons—were determined when packed in a number of types of solid and corrugated fibreboard cases during freezing at 0° F and thawing at 70° F. Fibreboard cases are generally used as shipping containers for the completely frozen food but may be desirable for use during the freezing of the chilled or partially frozen food. These tests were conducted to determine how the kind of case and the kind of small container affect their desirability for these purposes. Most of the cases tested were constructed to hold 24 one-pound containers in layers of twelve and were closed by sealing the flaps with silicate of soda supplemented by sealing the top and bottom center edges with gummed paper tape. The containers were filled with prune pulp and 40 per cent sugar sirup.

It was found that the position of the can in the case was more important in determining the rate of heat transfer than was the type of case studied. Thus, the cans in the top layer cooled more slowly during freezing and warmed faster during thawing than those in equivalent positions in the bottom layer. The differences observed between the rates of heat transfer into or from an exposed can in comparison with a can in a case were affected more by the influence of one can upon another than by the kind and thickness of the material forming the case. Each can in the case cooled more slowly than in the open air because of the heat radiated in the case from a neighboring can into the air space between them. Thus, the greater the number of neighboring cans surrounding a particular can, the slower was the rate of temperature change. This was true of the cans whether filled with prune pulp or with sirup. The results obtained with the tin cans were approximately duplicated by those obtained with Purity Paper Bottles, Tulip Nestrite cups, and Kleen Kup tubs. It was found that the rates of temperature change in fibreboard cases containing 24 packages each of the three types of paper container were for all practical purposes identical and not appreciably different from that found for cans.

The rate of temperature change at different points in a case solidly filled with one-pound butter cartons containing prune pulp was found to be dependent even to a greater extent than for other containers upon positions in the case.

A comparison of the slowest temperature changes in cans of prune pulp during freezing is shown in figure 5 for three of the cases tested. The differences shown between these cases are typical of those found for others. No marked differences were found between the various cases in their heat-insulating qualities during freezing and thawing.

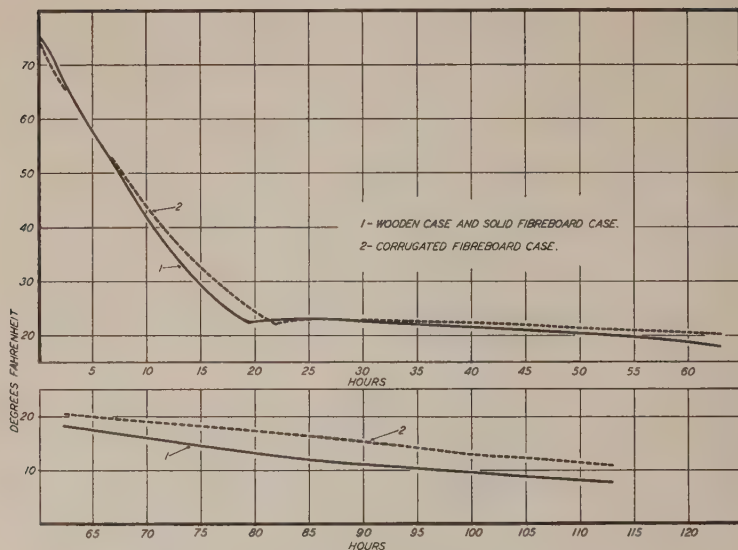


Fig. 5.—The slowest temperature changes in one-pound flat tins of prune pulp in several cases.

TABLE 5

COMPARISON OF RATES OF COOLING AND OF TEMPERATURE RISE AT VARIOUS LOCATIONS IN VARIOUS CASES

| Container  | Hours required to reach 23° Fahr. during freezing |              |              |              | Hours required to reach 23° Fahr. during thawing |              |              |              |
|--|---|--------------|--------------|--------------|--|--------------|--------------|--------------|
|  | Lower corner                                      | Lower center | Upper corner | Upper center | Lower corner                                     | Lower center | Upper corner | Upper center |
| 200-pound test R.S.C.* single-wall corrugated case.....  | 10  | 16           | 11           | 17½          | 10   | 18½          | 7½           | 15           |
| 200-pound test C.S.S.C.† single-wall corrugated case.....  | 10  | 15½          | 12½          | 17½          | 10   | 20           | 8            | 15           |
| 275-pound test R.S.C.* double-wall corrugated case.....  | 14  | 18½          | 15½          | 20½          | 11   | 20           | 8            | 15           |
| 275-pound test C.S.S.C.† double-wall corrugated case.....  | 14½   | 21           | 17           | 22           | 11½  | 21           | 8½           | 16½          |
| 275-pound test R.S.C.* double-wall corrugated case with double corrugated top and bottom pads and double corrugated liner..... | 19½   | 26           | 21           | 26½          | 13½  | 25½          | 9            | 19½          |
| 200-pound test C.S.S.C.† single-wall corrugated case with top and bottom pads and liners.....                                  | 15  | 20¾          | .....        | 21           | 16½  | 27½          | .....        | 22½          |

\* Regular slotted case.

† Center special slotted case.



Temperature changes in cans of 40 per cent sirup packed in six types of corrugated cases are summarized in table 5, and typical data are shown in figure 6. Here, also, there was no very marked difference between the various cases tested. Apparently, increasing the amount of packing material in the walls of the case did not have a pronounced effect under the conditions of our test. However, the generally used method

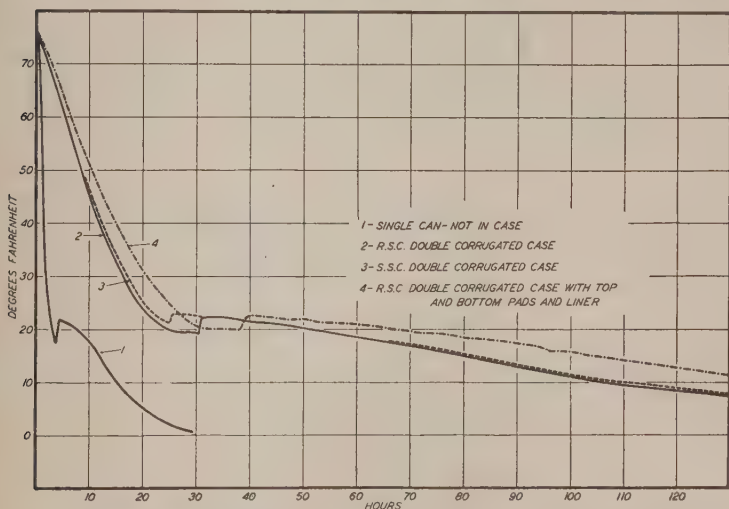


Fig. 6.—The slowest temperature changes during freezing in one-pound tin cans of 40 per cent sirup packed in various double-wall corrugated fibreboard cases. Temperature changes in a single can, not in case, are shown for comparison.

of further insulating the cases by the use of corrugated liners around the sides and ends may increase the insulation under certain conditions, especially where care is taken to reduce air leaks by thoroughly sealing the edges and corners.

These tests indicate that the behavior of the cases cannot be predicted from a knowledge of the general insulating qualities of the material forming the cases. The type and shape of the case, the nature of the material to be frozen or to be protected from thawing, and the type of individual container are apparently of more importance than the heat-insulating value of the walls of the case.

## CHANGES IN VOLUME ON FREEZING

Water, unlike most other liquids, expands on freezing. The increase in volume amounts to about 9 per cent. When water, fruit, fruit juices, and sirups are frozen in sealed containers, it is necessary to allow for the increase in volume on freezing in order to avoid the bursting of the containers.

Fresh fruits generally contain air in the intercellular spaces in which ice is first formed and when frozen at relatively high temperatures the fruits contract rather than expand in volume. However, when they are frozen at temperatures at which the entire fruit is rapidly frozen an expansion in volume occurs.

TABLE 6  
EXPANSION OF WATER AND SUGAR SOLUTIONS ON  
FREEZING

| Substance                       | Increase<br>in volume on<br>freezing at<br>0° to 5° F. in<br>per cent |
|---------------------------------|---|
| Water.....                      | 8.6   |
| 10 per cent sugar solution..... | 8.7   |
| 20 per cent sugar solution..... | 8.2   |
| 30 per cent sugar solution..... | 6.2   |
| 40 per cent sugar solution..... | 5.2   |
| 50 per cent sugar solution..... | 3.9   |
| 60 per cent sugar solution..... | None  |
| 70 per cent sugar solution..... | 1 per cent decrease<br>in volume                                      |

In determining changes in volume it was found expedient to cover the water, sirups, and fruit in sealed, tall, narrow cylinders with xylene since this procedure corrected for surface irregularities arising during freezing, such as bulging of the center, and incomplete fill, in case of the fruit. A correction was made for the decrease in volume of xylene at 0° to 5° F. Care was taken that the products should freeze from the bottom of the container upwards.

The increase in volume of sirups of various concentrations when prepared at room temperature and frozen at 0° to 5° F was determined with the results shown in table 6. These results are the average for ten determinations, which did not vary appreciably.

An average increase in volume of 4.0 per cent was found for whole raspberries frozen at 0° F, and of 6.3 per cent for crushed raspberries. At the same temperature whole strawberries increased 3.0 per cent,

strawberries with added sugar in the ratio of 2:1 increased 1.2 per cent, and crushed strawberries increased 8.2 per cent in volume. These results are averages of three to five determinations on the same lots of fruits.

Owing to the collapse of fruit, release of intercellular gases, and osmotic action of the added sugar or sirup, a decrease in volume occurs upon thawing. The volume occupied by the fruit subjected to freezing and thawing is considerably less than that occupied by the fresh fruit. The average decrease in volume of untreated strawberries was found to be about 6.8 per cent; of raspberries without sirup, 5.6 per cent; and 4.2 per cent for strawberries packed with sugar in the ratio of 2:1. This decrease is responsible for the apparent "slack fill" in containers of frozen-pack berries. These results represent actual changes in volume of the fruits.

Owing to shrinkage in volume upon thawing, a decrease in the depth of berries occurs. The reduction in depth is naturally more pronounced for whole untreated berries and less for berries packed in sirup. The apparent decrease in volume of blackberries, loganberries, raspberries, and strawberries in No. 10 friction-top cans upon thawing after freezing was found to be respectively 31.5, 27.8, 38.2, and 26.4 per cent. In berries packed in sirup the decrease in volume varied from none to 3 per cent and in berries packed with sugar it varied from 4 to 6 per cent, based on the initial volume before freezing.

#### CHANGES IN WEIGHT UPON THAWING

*Loss in Weight of Fruit Upon Thawing.*—A decrease in the weight of frozen fruit occurs during and after thawing. This decrease is due to the water separated as ice during freezing and not reabsorbed during thawing, to leakage of fluids through tissues injured by freezing, and to the osmotic action of the sugar or sirup. It does not depend entirely upon tissue disorganization, since it is offset in part by absorption of sugar in the case of sugar and sirup-pack fruits and depends to a large extent upon the handling of the product during thawing and draining. It is difficult to remove all of the added and exuded juice, sirup or water from the product by draining after thawing, although data so obtained are comparable.

The losses in weight of a number of fruits frozen in water and sirup, stored at 0° to 10° F for about a year, then allowed to thaw overnight for about 16 hours, and drained 2 minutes over a 1/8-inch mesh screen, are shown in table 7. With the exception of the results shown for No. 10 cans, the determinations were made at least in triplicate and in some



TABLE 7  
LOSS IN WEIGHT IN FRUITS PACKED IN WATER AND CANE SUGAR SIRUP

| Sample No. | Fruit                           | Container               | Ratio of fruit to sirup (approximate) | Per cent loss in weight of fruit packed in water and in sirups of Baling degree shown |          |          |          |          |          |          |          |
|------------|---------------------------------|-------------------------|---------------------------------------|---|----------|----------|----------|----------|----------|----------|----------|
|            |                                 |                         |                                       | Water   | 10° Bal. | 20° Bal. | 30° Bal. | 40° Bal. | 50° Bal. | 60° Bal. | 70° Bal. |
| 1          | Apricots, sliced                | Pint Tulip Nestrine cup | 275 grams fruit covered with sirup    | 21.0  |          | 18.5     |          | 22.9     | 22.7     | 20.8     |          |
| 2          | Apricots, halves                | Pint Tulip Nestrine cup | 275 grams fruit covered with sirup    |   |          |          | 13.2     |          |          |          |          |
| 3          | Apricots, quarters              | Pint Tulip Nestrine cup | 275 grams fruit covered with sirup    |   |          |          | 20.4     |          |          |          |          |
| 4          | Blackberries                    | No. 2 cans              | 1 : 1                                 | 32.0  |          | 22.8     |          |          |          | 19.4     |          |
| 5          | Blackberries                    | No. 10 cans             | 1½ : 1                                |   |          |          |          | 12.7     |          |          |          |
| 6          | Loganberries                    | No. 10 cans             | 1½ : 1                                |   |          |          |          | 27.2     |          |          |          |
| 7          | Peaches, Phillips Cling, halves | Pint Kleen Kup          | 1 : 1½                                |   |          | 0.7      |          | 3.9      | 8.3      | 12.9     | 32.3     |
| 8          | Peaches, Phillips Cling, halves | 5-gallon can            | 21.5 pounds fruit covered with sirup  |   |          |          | 13.8     | 19.3     | 18.3     |          | 21.8     |
| 9          | Peaches, Lovell, sliced         | 8-ounce can             | 1½ : 1                                | 17.8  | 23.2     |          |          |          |          |          |          |
| 10         | Peaches, Phillips Cling, sliced | No. 2 can               | 1½ : 1                                | 30.2  | 9.3      |          | 10.7     | 10.7     | 11.8     |          | 26.8     |
| 11         | Raspberries                     | No. 10 can              | 1½ : 1                                |   |          |          |          | 21.5     |          |          |          |
| 12         | Strawberries, Banner (1929)     | Pint Tulip Nestrine cup | 250 grams fruit covered with sirup    | 46.4  | 44.8     | 35.6     | 45.4     | 16.8     | 30.7     | 26.8     | 22.0     |
| 13         | Strawberries, Banner (1929)     | No. 2 can               | 1 : 1½                                |   |          |          |          | 40.2     |          | 33.6     | 35.9     |
| 14         | Strawberries, Banner (1930)*    | Pint Tulip Nestrine cup | 1 : 2                                 | 23.9  | 35.1     | 8.0      | 13.7     | 14.4     | 7.4      | 12.6     | 9.0      |
| 15         | Strawberries, Banner (1931)     | Pint Kleen Kup          | 1½ : 1                                |   | 37.4     | 34.1     | 27.5     | 29.1     | 26.5     | 31.7     |          |
| 16         | Strawberries, Banner (1930)     | No. 10 cans             | 1,800 grams fruit to 500 cc sirup     | 34.4  |          | 38.3     |          | 32.0     | 36.1     | 33.6     | 44.2     |
| 17         | Youngberries, green             | Quart jars              | 1 : 1                                 |   |          |          |          | 18.6     |          |          |          |
| 18         | Youngberries, green             | Pint jars               | 1 : 1                                 |   |          |          |          | 13.7     |          |          |          |
| 19         | Youngberries, ripe              | Pint jars               | 1 : 1                                 |   |          |          |          | 16.5     |          |          |          |

\* Unhulled berries.

cases the results shown are averages of ten determinations. All fruit was purchased from the commission merchants in Oakland, and was fresh fruit of good quality. An effort was made to secure representative samples of fruit by thoroughly mixing the fruit where possible, *en masse*, or by random selection. The differences between samples packed in sirup of a given concentration were closer than between samples packed in sirups of different concentrations. However, the fruits used were rather variable, as the results for successive years in certain cases indicate, but

TABLE 8

BALLING DEGREE OF DRAINED SIRUPS FROM FRUITS PACKED IN WATER AND SIRUPS OF DIFFERENT CONCENTRATIONS

| Sample No. | Water | 10° Bal. | 20° Bal. | 30° Bal. | 40° Bal. | 50° Bal. | 60° Bal. | 70° Bal. |
|------------|-------|----------|----------|----------|----------|----------|----------|----------|
| 1          | 11.6  | .....    | 17.6     | .....    | 25.6     | 26.3     | 36.5     | .....    |
| 2          | ..... | .....    | .....    | .....    | 21.7     | .....    | .....    | .....    |
| 3          | ..... | .....    | .....    | .....    | 25.2     | .....    | .....    | .....    |
| 4          | 5.9   | .....    | 16.3     | .....    | 32.0     | .....    | 44.0     | .....    |
| 5          | ..... | .....    | .....    | .....    | 28.4     | .....    | .....    | .....    |
| 6          | ..... | .....    | .....    | .....    | 27.4     | .....    | .....    | .....    |
| 7          | ..... | .....    | 19.0     | .....    | 36.0     | 42.5     | 50.5     | 52.0*    |
| 8          | ..... | .....    | .....    | .....    | 30.0     | 37.5     | .....    | .....    |
| 9          | 10.5  | 16.5     | .....    | 23.2     | 30.3     | 34.5     | .....    | 42.9     |
| 10         | 7.6   | 12.2     | .....    | 22.4     | 25.2     | .....    | .....    | .....    |
| 11         | ..... | .....    | .....    | .....    | 23.0     | .....    | .....    | .....    |
| 12         | 4.8   | 8.2      | 14.6     | 20.6     | 23.2     | 30.4     | 38.2     | 42.0     |
| 13         | ..... | .....    | .....    | .....    | 30.5     | .....    | 42.0     | 50.2     |
| 14         | 4.5   | 11.3     | 18.4     | 25.5     | 32.2     | 41.0     | 48.0     | 54.0     |
| 15         | ..... | 12.5     | 17.8     | 23.1     | 27.8     | 33.1     | 40.7     | .....    |
| 16         | 7.0   | .....    | 13.8     | .....    | 23.8     | 27.8     | 31.4     | 41.4     |
| 17         | ..... | .....    | .....    | .....    | 29.6     | .....    | .....    | .....    |
| 18         | ..... | .....    | .....    | .....    | 31.7     | .....    | .....    | .....    |
| 19         | ..... | .....    | .....    | .....    | 31.1     | .....    | .....    | .....    |

\* Undissolved sugar present.

the trend was in the same direction. In general, the loss reported varied with the kind and character of fruit and was greatest in water and least in sirups of certain concentrations. The change in Balling degree of sirup as shown in table 8 was greater where the change in weight as shown in table 7 was greater. The loss in weight as a result of the freezing and thawing did not vary in a regular manner with the concentration of sirup and there was no definite relation, such as would be expected, between loss in weight and concentration of sirup, if osmotic action alone had been responsible for the loss in weight. These results are similar to those reported by Wiegand<sup>(12)</sup> for berries.

However, osmotic action of the sirup as demonstrated in work reported by the senior author elsewhere<sup>(7)</sup> plays an important rôle in the

extraction of water from the fruit when stored at room temperature. Fruits packed in water or dilute sirup generally gain weight while those packed in concentrated sirups lose weight. The average loss in weight of peaches increased with increase in concentration of sirup and with the length of time the sirup was allowed to stand in contact with the fruit. Equilibrium was not attained at room temperature even after 28 hours. The series was discontinued at 28 hours owing to incipient fermentation. The loss in weight upon freezing and subsequent thawing for 11 hours was less than the loss after 28 hours at room temperature. An increase in weight occurred in peaches stored in 22.5° Balling sirup

TABLE 9  
BALLING DEGREE OF LIQUID AND LOSS IN WEIGHT OF  
BERRIES PACKED WITHOUT SUGAR OR SIRUP

| Fruit                     | Loss<br>in weight,<br>per cent | Balling<br>degree of<br>liquid |
|---------------------------|--------------------------------|--------------------------------|
| Blackberries (1929).....  | 37.6                           | 15.0                           |
| Blackberries (1930)*..... | 15.7                           | 14.5                           |
| Loganberries*.....        | 27.2                           | 10.0                           |
| Raspberries*.....         | 32.5                           | 8.0                            |
| Strawberries*.....        | 34.5                           | 10.8                           |
| Strawberries.....         | 36.6                           | 9.4                            |
| Youngberries.....         | 27.5                           | 7.6                            |
| Youngberries.....         | 23.5                           | 10.8                           |

\* Packed in No. 10 cans while the others were in small containers.

at room temperature owing either to absorption of sirup or to incomplete draining. Similar results were found for strawberries, in which the absorption of water or sirup was very marked.

In a subsequent investigation it was found that the average loss in weight of lye-peeled, halved, Phillips Cling peaches at 68° F and 32° F increased with increase in concentration of the sirup, being greater in 60° and in 40° Balling sirup than in 25° sirup. The loss in weight became constant after about 48 hours at 68° F and after 100 to 150 hours at 32° F. The equilibrium was established more quickly in sirups of lower concentration.

Although the loss of weight of fruit stored in sirup at room temperature may be due almost entirely to drawing of water from the fruit tissues by osmosis, the situation is different with fruit frozen without added sugar or sirup. As a result of injury to the tissues during freezing, juice or cell sap exudes during thawing as shown for berries in table 9. This may be owing in part to mechanical injury to the tissues;



in part to the osmotic indifference, that is, loss by the cells of their property or semipermeability; and in part to change of gels present to more dehydrated gels and sols. Similar conditions—modified, in degree but not in kind, by the sugar or sirup present—probably occur in fruits frozen with sugar or in sirup. It is believed by the writers that the loss in weight that occurs upon thawing is due not only to water extracted by the osmotic action of the sugar or sirup but also to loss of juice that exudes as a result of injury to the tissues on freezing. However, Diehl *et al.*<sup>(3)</sup> apparently favors the view that a withdrawal of water only occurs in fruit frozen with sugar and that this is brought about by the osmotic action of the sugar.

*Effect of Ratio of Fruit to Sugar and of Kind of Sugar.*—The losses in weight of apricots and berries packed with varying amounts of sugar and with different kinds of sugar are shown in table 10. These are aver-

TABLE 10

AVERAGE LOSS IN WEIGHT OF APRICOTS AND BERRIES PACKED WITH DIFFERENT PROPORTIONS OF SUGAR

| Fruit                     | Sugar           | Percentage loss in weight |       |       |       |       | Balling degree of drained sirup |       |       |       |       |
|---------------------------|-----------------|---------------------------|-------|-------|-------|-------|---------------------------------|-------|-------|-------|-------|
|                           |                 | 1:1                       | 2:1   | 3:1   | 4:1   | 5:1   | 1:1                             | 2:1   | 3:1   | 4:1   | 5:1   |
| Apricots, sliced.....     | Cane.....       | .....                     | ..... | 13.6  | 10.0  | 2.0   | .....                           | ..... | ..... | ..... | ..... |
|                           | Cane.....       | .....                     | 23.6  | 3.0   | ..... | ..... | .....                           | ..... | ..... | ..... | ..... |
| 1929                      | Cane.....       | 19.4*                     | 30.9  | 36.5  | 34.5  | ..... | 56.5                            | 43.3  | 35.0  | 30.8  | ..... |
| 1929                      | Cerelose.....   | 23.2*                     | 36.0* | 42.4  | ..... | ..... | 47.5                            | 39.4  | 28.3  | ..... | ..... |
| Strawberries, Banner..... | Cane.....       | .....                     | 35.8  | 36.2  | 40.7  | 44.2  | .....                           | 51.0  | 39.2  | 27.5  | 22.8  |
| 1930                      | Cane.....       | .....                     | ..... | 38.8  | ..... | ..... | .....                           | 47.4  | ..... | ..... | ..... |
| 1931                      | Cane.....       | .....                     | ..... | ..... | ..... | ..... | .....                           | ..... | ..... | ..... | ..... |
| 1931                      | Cane.....       | 38.5                      | 34.6  | 35.4  | 38.0  | 34.7  | 67.4                            | 51.3  | 43.8  | 33.8  | 31.0  |
| 1931                      | Invert.....     | 31.6                      | 36.4  | 30.5  | 30.0  | 34.5  | 56.3                            | 44.2  | 37.3  | 32.3  | 28.2  |
| Youngberries, 1930.....   | Ripe Cane.....  | .....                     | ..... | 24.9  | ..... | ..... | .....                           | ..... | 35.9  | ..... | ..... |
|                           | Green Cane..... | .....                     | ..... | 22.6  | ..... | ..... | .....                           | ..... | 48.2  | ..... | ..... |

\* Sugar separated.

ages of triplicate determinations. The loss in weight of apricots decreased with increase in the ratio of fruit to added cane sugar but the results for Banner strawberries were rather variable. The substitution of cerelose for cane sugar increased the loss in weight to some extent. The substitution of invert sugar testing 76.3° Balling also decreased the loss in weight. However, in these tests there was no direct relation between the ratio of fruit to sugar and the loss in weight. The data reported by Wiegand<sup>(12)</sup> indicate that in some instances the loss in weight of berries frozen with sugar increased as the ratio of fruit to sugar decreased and in others there was no continuous and regular increase.

Diehl *et al.*<sup>(3)</sup> report that an increase in the concentration of cane sugar resulted in an increase in the amount of water extracted as shown by increased percentages of soluble solids in the fruit.

A further comparison between invert and cane sugar, made up in sirups, is shown in table 11. The increase in loss in weight of strawberries which occurred in some but not all of the concentrations of sirups used as given in the table, however, was not as large as would be ex-

TABLE 11  
COMPARISON OF LOSS IN WEIGHT OF  
BANNER STRAWBERRIES IN CANE-  
SUGAR SIRUP AND IN INVERT-  
SUGAR SIRUP

| Balling<br>degree of<br>sirup | Percentage loss in weight |                       |
|-------------------------------|---------------------------|-----------------------|
|                               | Cane-sugar<br>sirup       | Invert-sugar<br>sirup |
| 10                            | 37.4                      | 34.3                  |
| 20                            | 34.1                      | 31.3                  |
| 30                            | 27.5                      | 30.2                  |
| 40                            | 29.1                      | 29.3                  |
| 50                            | 26.5                      | 27.8                  |
| 60                            | 31.7                      | 28.8                  |
| 65                            | 26.2                      | 32.3                  |

pected from the molecular size of the two sugars. The osmotic pressure of invert sugar sirup is roughly twice that of cane-sugar sirup. Apparently other factors besides osmotic pressure are involved in loss in weight upon thawing.

Similar erratic results were obtained in a test with sliced Phillips Cling peaches; in two cases the loss in weight in invert sugar-sirup solutions was about three times that in cane-sugar solutions of the same concentration, but in other cases the loss in weight in invert-sugar sirup was less than in cane-sugar sirup.

*Effect of Variety of Fruit on Loss in Weight.*—The average loss in weight after freezing and thawing in four varieties of strawberries commercially grown in California is shown in table 12. Duplicate portions of these berries were frozen as follows: in sirup of 40° Balling, with sugar, and without either sirup or sugar added. They were stored for 6 months at 0° to 10° F, thawed at room temperature overnight for about 16 hours, and then drained for 2 minutes over a 1/8-inch mesh screen. The loss in weight of berries frozen in sirup was least for Nich Ohmer and greatest for Molinda. The loss in weight of the berries frozen

with sugar was least for Capitola and greatest for Molinda. However, since berries are variable in structure and composition, depending upon maturity, too much significance should not be attached to the results of this one year's test.

The average loss in weight of a number of varieties of peaches is shown in table 12. It was less than for strawberries and not markedly

TABLE 12  
EFFECT OF VARIETY OF FRUIT UPON LOSS IN WEIGHT

| Variety                | Treatment   | Balling degree of drained sirup | Percentage loss in weight |
|------------------------|---|---------------------------------|---------------------------|
| Strawberries:          |   |                                 |                           |
| Banner.....            | Packed in 40° Balling cane sugar sirup.....         | 26.6                            | 25.6                      |
| Capitola.....          | Packed in 40° Balling cane sugar sirup.....         | 30.8                            | 19.5                      |
| Molinda.....           | Packed in 40° Balling cane sugar sirup.....         | 26.8                            | 30.7                      |
| Nich Ohmer.....        | Packed in 40° Balling cane sugar sirup.....         | 28.4                            | 15.6                      |
| Banner.....            | 3 : 1 cane sugar pack.....                          | 35.0                            | 26.8                      |
| Capitola.....          | 3 : 1 cane sugar pack.....                          | 36.0                            | 21.3                      |
| Molinda.....           | 3 : 1 cane sugar pack.....                          | 37.0                            | 27.7                      |
| Nich Ohmer.....        | 3 : 1 cane sugar pack.....                          | 35.6                            | 24.1                      |
| Capitola.....          | Untreated.....                                      | 7.8                             | 34.7                      |
| Nich Ohmer.....        | Untreated.....                                      | 8.2                             | 44.0                      |
| Peaches:               |   |                                 |                           |
| Orange Cling.....      | Sliced; packed in 40° Balling cane sugar sirup..... | 28.1                            | 13.1                      |
| Sims (green ripe)..... | Sliced; packed in 40° Balling cane sugar sirup..... | 28.3                            | 7.8                       |
| Sims (ripe).....       | Sliced; packed in 40° Balling cane sugar sirup..... | 26.3                            | 9.3                       |
| Phillips Cling.....    | Sliced; packed in 40° Balling cane sugar sirup..... | 24.2                            | 11.1                      |
| Lovell.....            | Sliced; packed in 40° Balling cane sugar sirup..... | 26.3                            | 12.2                      |
| Salwey.....            | Sliced; packed in 40° Balling cane sugar sirup..... | 30.1                            | 13.7                      |

different for the varieties used. However, with the exception of ripe Orange Cling peaches the loss in weight of the freestone varieties was somewhat higher than for the clingstone varieties.

*Change in Weight in Vegetables Upon Thawing.*—The change in weight of frozen vegetables upon thawing as shown in table 13 depends upon the kind of vegetable, treatment prior to freezing, and upon whether or not the vegetable is packed in brine. In most cases, the change in weight was a decrease, but in some instances an increase occurred in the weight of blanched vegetables frozen in brine. This increase was more marked as the rate of freezing was increased. In general, blanching the vegetables increased the loss in weight and freezing in brine decreased the loss in weight. Of the vegetables tested the loss in weight for asparagus stalks was greatest and that for artichokes least. The results reported, except for No. 10 cans, are averages of triplicate determinations for vegetables purchased in the Oakland markets.

TABLE 13  
CHANGE IN WEIGHT OF FROZEN VEGETABLES UPON THAWING

| Vegetable                    | Treatment  | Percentage loss in weight |
|------------------------------|--|---------------------------|
| Artichokes.....              | Plain; blanched in water, steam, or acid brine; packed with and without brine..... | 0.0                       |
| Asparagus, white (1928)..... | { Untreated.....   | 20.9                      |
|                              | { Blanched in water; no brine added.....   | 22.7                      |
|                              | { Blanched in water; 2.5% brine added to cover.....                                | 20.0                      |
|                              | { Blanched in water; 5% brine added to cover.....                                  | 27.9                      |
|                              | { Blanched in steam; 2.5% brine added to cover.....                                | 26.3                      |
|                              | { Blanched in steam; 5% brine added to cover.....                                  | 30.7                      |
|                              | { Blanched in 1% citric acid; no brine added.....                                  | 17.2                      |
|                              | { Blanched in 1% citric acid; 2.5% brine added to cover.....                       | 10.0                      |
| Asparagus, green (1928)..... | { Blanched in 1% citric acid; 5% brine added to cover..                            | 30.8                      |
|                              | { Blanched in water; no brine added.....   | 23.1                      |
|                              | { Blanched in water; 2.5% brine added to cover.....                                | 19.3                      |
|                              | { Blanched in water; 5% brine added to cover.....                                  | 29.7                      |
|                              | { Blanched in steam; no brine added.....   | 6.8                       |
| Asparagus, white (1930)..... | { Blanched in steam; 5% brine added to cover.....                                  | 15.9                      |
|                              | { Untreated.....   | 13.10                     |
|                              | { Untreated; 5% brine added to cover.....  | 11.3                      |
|                              | { Blanched in steam; no brine added.....   | 9.65                      |
| Asparagus, white (1931)..... | { Blanched in steam; 5% brine added to cover.....                                  | 0.11 (gain)               |
|                              | { Untreated.....   | 23.4                      |
|                              | { Untreated; 2% brine added to cover.....  | 11.1                      |
|                              | { Blanched in steam; no brine added.....   | 25.2                      |
| Corn.....                    | { Blanched in steam; 2% brine added to cover.....                                  | 10.5                      |
|                              | { Golden Bantam on cob; blanched in steam; 2% brine added to cover.....            | 8.5                       |
| Peas, shelled (1930).....    | { Untreated.....   | 9.14                      |
|                              | { Untreated; 5% brine added to cover.....  | 7.35                      |
| Peas, shelled (1931).....    | { Untreated.....   | 8.3                       |
|                              | { Untreated; 2% brine added to cover.....  | 6.3                       |
|                              | { Blanched in steam; no brine added.....   | 6.6                       |
|                              | { Blanched in steam; 2% brine added to cover.....                                  | 2.7 (gain)                |
| String beans (1930).....     | { Untreated.....   | 3.75                      |
|                              | { Untreated; 5% brine added to cover.....  | 0.10                      |
|                              | { Blanched in water; no brine added.....   | 6.08                      |
|                              | { Blanched in water; 5% brine added to cover.....                                  | 2.36                      |
| String beans (1931).....     | { Untreated.....   | 14.5                      |
|                              | { Untreated; 2% brine added to cover.....  | 18.9                      |
|                              | { Blanched in steam; no brine added.....   | 13.8                      |
|                              | { Blanched in steam; 2% brine added.....   | 13.4                      |
| Spinach.....                 | { Untreated.....   | 0.0                       |
|                              | { Untreated; 5% brine added to cover.....  | 16.5 (gain)               |
|                              | { Blanched in water; no brine added.....   | 7.0                       |
|                              | { Blanched in water; 2% brine added to cover.....                                  | 7.4 (gain)                |



*Effect of Rate of Freezing Upon Change in Weight.*—In March, 1931, early string beans of fair quality from Mexico, early peas of good quality, and fresh white asparagus, were frozen in still air at 0° F, in brine at 0° F, and in solid carbon dioxide ("dry ice"). Some were blanched, others were not blanched, and were packed with and without brine. The asparagus was cut to 4-inch lengths and packed in No. 2 cans; the cut string beans and the shelled peas were packed in one-pound flat tin cans. The determinations were made in triplicate. The average losses in weight upon thawing after storage for more than a year at 0° to 10° F are shown in table 14. It is seen that the loss decreased as the rate of

TABLE 14  
EFFECT OF RATE FREEZING ON LOSS OF WEIGHT IN VEGETABLES

| Treatment                                      | Refrigerant            | Percentage loss in weight |       |              |
|--|------------------------|---------------------------|-------|--------------|
|  |                        | Asparagus                 | Peas  | String beans |
| Untreated; no brine added.....                 | Still air at 0° F..... | 23.4                      | 8.4   | 14.5         |
|  | Brine at 0° F.....     | .....                     | 8.5   | 11.6         |
|  | Dry ice at -110° F.... | 19.2                      | 4.5   | 8.2          |
| Untreated; 2% brine added to cover {           | Still air at 0° F..... | 11.1                      | 6.3   | 19.4         |
|  | Brine at 0° F.....     | .....                     | 6.9   | 8.3          |
|  | Dry ice at -110° F.... | 3.4                       | 1.6   | 1.5          |
| Steam blanched; no brine added... {            | Still air at 0° F..... | 25.2                      | 6.6   | 13.8         |
|  | Brine at 0° F.....     | .....                     | 3.4   | 10.1         |
|  | Dry ice at -110° F.... | 14.4                      | 0.6   | 6.8          |
| Steam blanched; 2% brine added to cover..... { | Still air at 0° F..... | 10.5                      | -2.7* | 13.4         |
|  | Brine at 0° F.....     | .....                     | -1.8* | 3.8          |
|  | Dry ice at -110° F.... | -3.3*                     | -7.1* | -3.8*        |

\* Indicates gain in weight.

freezing increased. This was especially marked for vegetables frozen with brine added as compared with vegetables with no brine.

In another test it was found that whole Alameda Trophy tomatoes frozen in dry ice and then stored at 0° to 10° F for a year in hermetically sealed cans did not lose as much weight upon thawing as did those frozen in air at 0° F.

In still another test a number of untreated vegetables and certain fruits were frozen in air at 0° F and in dry ice. The loss in weight upon thawing, after storage for two weeks at 0° F, was determined and it was found that the initial rapid freezing decreased the leakage somewhat; but this decrease was not very marked except for asparagus butts. These results confirm those by Woodroof<sup>(14)</sup> who reported that the loss in weight of quick-frozen sliced tomatoes, Hale peaches, bananas, and pears was less than that for similar products slow frozen.

*Relations of Loss in Weight to Texture.*—The free drip or loss in weight during thawing has often been used as an acceptable index of the change in the colloidal state and degree of disorganization of flesh products. Woodroof<sup>(14)</sup> reported that "the quantity of fluid lost by the cell through leakage to the outside, loss of original turgidity and degree of fragmentation of the precipitated protoplasm were in direct proportion." We found that, in general, there is a complete loss of crispness upon freezing; the juicy portions become soft and flabby, and the fibrous portions become tough. There is not an even distribution of tenderness such as has been reported for flesh products. There is some relation between the degree of retention of original shape and turgidity and loss in weight. The greater the loss in weight, the more severely is the texture disorganized. Fruits packed in sirup retain their structure better than those packed with dry sugar,<sup>(2, 3, 5, 6, 8, 11)</sup> even though the loss in weight for the latter may be less. It has been our experience that, with the possible exception of asparagus, increasing the rate of freezing by using solid carbon dioxide does not appreciably improve the texture of frozen fruits and vegetables examined. However, the addition of sirup to fruit or of brine to vegetables to be preserved by freezing markedly decreases the degree of breakdown in texture.

*"Sugar Curing."*—Although storing Banner strawberries and Phillips peaches in sirup or with sugar for 24 to 48 hours at 32° F prior to freezing in air at 0° F decreased the loss in weight, especially in the sugar-packed fruit, the texture was not materially improved. Wiegand<sup>(12)</sup> reported that Oregon (Marshall) strawberries held in sirup or with sugar at 30° to 31° F for 24 to 72 hours before freezing were superior in color, flavor, and texture to those frozen without such treatment. His results indicate that osmotic equilibrium in sirup and sugar-packed Clark seedling strawberries is reached in about 24 hours at 30° to 31° F. We found that Banner strawberries and Phillips Cling peaches held in sirup or with sugar for 24 to 48 hours at 32° F prior to freezing were not materially improved in texture over similar fruits frozen immediately. However, the loss in weight of the sugar-cured fruit was less than that in fruit frozen without such storage. In a subsequent communication, Professor Wiegand reports that storage for at least 48 hours at 32° F prior to freezing was necessary to obtain the desired effect of sugar curing.

## CHANGES IN PECTIN CONTENT ON FREEZING

The change in pectin content in blackberries during freezing was determined as follows. As a control or check, one lot of blackberries was crushed, heated to boiling in 8 minutes, boiled 3 minutes, cooled, brought to original weight by addition of water, pressed in a hand press, and the extracted juice pasteurized for 25 minutes at 175° F. One lot of whole and one of crushed berries were stored at 0° to 5° F for a period of 18 days, then allowed to thaw for 24 hours at room temperature and were then treated as previously described for the check lot. The pectic acid content of these samples was determined with the following results. The

TABLE 15  
CHANGES IN PECTIC ACID CONTENT OF BLACKBERRIES  
AFTER FREEZING AND THAWING

| Sample and treatment  | Grams pectic acid<br>per 25 cc of<br>original juice* |
|---|--|
| Check.....  | 0.079  |
| Crushed and stored at 0° F.....   | 0.048  |
| Whole, stored at 0° F.....  | 0.048  |
| Whole, 1,500 grams with 1,000 grams water and<br>stored at 0° F.....        | 0.058  |
| Whole, 1,500 grams with 1,000 grams of 40% sirup<br>and stored at 0° F..... | 0.050  |
| Whole, with added sugar, 2 fl.....  | 0.044  |

\* This is after correcting for dilution of pectin in the original juice by the addition of water, sugar, or sirup.

juice from the check lot contained 0.05 gram pectic acid per 25 cc of juice; that from whole, frozen berries, 0.049 gram; and that from crushed, frozen berries, 0.055 gram.

Another set of samples was prepared and the pectic acid content of the expressed juice was determined as above after storage for one month. The results of this test are shown in table 15. They are averages of closely agreeing duplicate determinations.

Owing to the difficulty of controlling the conditions of extracting the juice from the berries, the results were not entirely consistent. Apparently, however, the loss in pectin on freezing is not large. The jellying power of the berry juice as shown by jellying tests was not markedly affected by freezing, storage, and thawing. Diehl *et al.*<sup>(3)</sup> working with large quantities found that loss in pectin content of raspberries and strawberries occurred in a few instances, but believed that this loss was due to the longer period of time required to freeze the fruit mass in quantity.

### INVERSION OF SUCROSE BY NATURALLY OCCURRING OR ADDED ENZYMES

In order to determine the extent of inversion of sucrose by the naturally occurring enzymes in certain fruits, partially crushed Banner strawberries, Cuthbert raspberries, and crushed clingstone peaches were mixed with definite, known proportions of sucrose and stored at about 0° F as described below; they were then analyzed for reducing sugar before and after inversion with acid.

The strawberries and raspberries were stored for a period of two years, during which time they were subjected to marked fluctuations in temperature, being exposed to as high as 25° F for several days. The

TABLE 16  
EXTENT OF INVERSION OF SUCROSE IN RASPBERRIES AND STRAWBERRIES FROZEN WITH  
ADDED SUCROSE

| Ratio of fruit<br>to sugar | Per cent sucrose inverted |              | Ratio of fruit<br>to sugar | Per cent sucrose inverted |              |
|----------------------------|---------------------------|--------------|----------------------------|---------------------------|--------------|
|                            | Rapid thawing             | Slow thawing |                            | Rapid thawing             | Slow thawing |
| <i>Raspberries</i>         |                           |              | <i>Strawberries</i>        |                           |              |
| No sucrose added.....      | 100.0                     | 100.0        | No sucrose added.....      | 100.0                     | 100.0        |
| 1 : 1.....                 | 14.4                      | 17.2         | 1 : 1.....                 | 26.0                      | 36.6         |
| 2 : 1.....                 | .....                     | 30.0         | 2 : 1.....                 | 42.0                      | 64.6         |
| 3 : 1.....                 | 32.4                      | 48.8         | 3 : 1.....                 | 56.0                      | 83.3         |
| 4 : 1.....                 | 15.5                      | 50.0         | 4 : 1.....                 | 68.5                      | 87.1         |
| 5 : 1.....                 | 24.0                      | 56.8         | 5 : 1.....                 | 82.1                      | 83.0         |

berries were removed from storage and one lot thawed by setting in boiling water and another allowed to thaw for 48 hours at room temperature. After thawing, the entire contents of the cans were boiled for one-half to one hour in distilled water adjusted to a pH of 6.8 to reduce inversion of sucrose by acid during extraction. The reducing and total sugars in the extract were determined after clarification by the Shaffer and Hartmann method. The results are shown in table 16. It is seen that a considerable inversion of the added sucrose occurred, being more marked with strawberries than with raspberries. A certain loss of added sucrose occurred, which might have been due to the activity of micro-organisms. The per cent of sucrose inverted increased with decrease in amount of added sugar and increased upon prolonging the thawing period.

Ripe Sims clingstone and Orange Cling peaches were ground, mixed with varying amounts of sugar and stored at 0° to 5° F for a period of



about eight months. These samples were allowed to thaw for 16 hours at room temperature; after which they were extracted and analyzed. The results found indicate practically no inversion of added sucrose. A slight amount of inverted sucrose was found in the lot that was sterilized by heating for one hour at  $212^{\circ}$  F prior to freezing, but this was probably formed by inversion during heating. It is worthy of note that the untreated peaches contained a large proportion of sucrose, whereas no sucrose was found in the berries.

There is some evidence that persimmons contain an active invertase since no sucrose was found in extracts prepared from persimmon pulp frozen with varying amounts of added sucrose after storage for one year. The extracts were stored at  $32^{\circ}$  F and protected with added toluene for a number of months prior to analysis.

These preliminary investigations having shown that inversion of pure sucrose occurred in the presence of invertase during freezing storage, this point was investigated further. A number of samples of sucrose solution of different concentrations were prepared, chilled to about  $35^{\circ}$  F, and adjusted to a pH of approximately 4.5 with acetic acid. They were then divided into equal portions and mixed with such quantities of chilled invertase solutions that the resultant mixed samples contained respectively 0.05, 0.01, and 0.001 mg of pure dry invertase in the form known as invertase "scales" (free from melibiase), per cubic centimeter of solution. The completed samples were then quickly poured into chilled bottles, sealed at once, and immediately placed in the freezing room at about  $3^{\circ}$  F. Two sets of samples were placed in a refrigerator and cooled to about  $-40^{\circ}$  F with dry ice. One complete set of samples was removed from the freezing room a few hours after sealing, made alkaline with ammonia while being thawed, and polarized in normal-weight solution. Previous investigations had shown that invertase is sufficiently inactivated by ammonia to permit polarization at room temperature without material error. This set of samples served as the control. At various intervals of about 2, 4, and 8 weeks sets of samples were removed from storage and the sugars present determined by polarization as before.

It was found that sucrose was appreciably inverted at temperatures of  $0^{\circ}$  to  $5^{\circ}$  F by invertase in concentrations as low as 0.001 mg per cubic centimeter in as little as 250 hours at the optimum pH of the enzyme. The per cent of inversion increased with time and concentration of enzyme, and increased also with decrease in concentration of sucrose in solution.

It was found that at the end of two months practically no sucrose was inverted in the samples stored at about  $-40^{\circ}$  F. The rate of inversion of sucrose by invertase at low temperatures is being investigated further.

### ABSORPTION OF SUGAR BY FRUIT

Fruits are generally frozen with sugar or sirup and, as will be shown, a portion of the sugar added as such or in the sirup is absorbed by the fruit during freezing and subsequent thawing. The amount of sugar absorbed can be shown in a number of ways. Assuming that the loss in weight after freezing and subsequent thawing is due to loss of water from, and gain in sugar by, the fruit, the amount of sugar absorbed can be calculated from an accurate estimate of loss in weight of fruit and increase in weight and change in composition of the sirup. However, this method may not be exact owing to the difficulty of completely draining the fruit and to the fact that the simple mechanism postulated above may not hold. It is possible that the cells of fresh fruits are impermeable to sugars and other soluble solids in the cell sap but permeable to water so that only water is extracted by the osmotic action of the added sugar or sirup. However, this selective permeability is destroyed by the killing action of freezing temperatures and the fruit becomes osmotically indifferent so that loss of soluble solids as well as water occurs during thawing. The gels present in the fresh fruit are probably changed to sols upon freezing and leak out as such through ruptured tissues during thawing. Assuming that juice and not water is lost, any increase in the concentration of soluble solids present in the fruit tissue is an indication of sugar absorption. Finally, an analysis of the fruit tissues washed with an isotonic solution of salt will indicate the degree of absorption of sucrose although the presence of an active invertase may interfere with this determination.

An application of one of the last two methods was made as follows: Sliced Lovell peaches packed in sirups of varying concentrations were frozen at  $0^{\circ}$  to  $5^{\circ}$  F and stored for a period of eight months in sealed 8-ounce cans, then thawed at room temperature for 16 hours. The sugar content of the sirup and peach tissue, washed free of adhering sirup with a 5 per cent salt solution,<sup>6</sup> was determined by the Shaffer and Hartmann method before and after acid inversion in the cold. The refractive index of the sirup, and of the juice pressed from the peach tissue, was determined, and the corresponding per cents soluble solids as sugars

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<sup>6</sup> The use of an isotonic salt solution for this purpose was suggested to us by H. C. Diehl.

were obtained from tables. It was found that the sucrose content of the peach tissue increased markedly with increase in concentration of sirup although the reducing sugars remained practically constant, thus indicating definite sugar absorption. Similar results were obtained with sliced Phillips Cling peaches. The sugar concentrations determined by refractometer were of the same order of magnitude, but apparently certain discrepancies entered because in a number of samples higher percentage of sugar was found in the flesh than in the sirup. Further work on this point is now in progress.

TABLE 17  
CALCULATED SUGAR ABSORPTION BY "SUGAR CURED" BANNER STRAWBERRIES

|  | Stored at<br>0° Fahr. immediately after<br>preparation |  | Stored at 32° Fahr.<br>for 24 hours prior to storage<br>at 0° Fahr. |  |
|--|--|--|---|--|
|  | Packed in<br>50° Balling<br>cane sugar<br>sirup        | Packed<br>with dry cane<br>sugar in<br>2 : 1 ratio | Packed in<br>50° Balling<br>cane sugar<br>sirup                     | Packed<br>with dry cane<br>sugar in<br>2 : 1 ratio |
| Before freezing:                         |  |  |   |  |
| Weight of berries, grams.....            | 242.7  | 243.0  | 241.8   | 241.5  |
| Weight of sirup or sugar, grams.....     | 161.7  | 122.0  | 161.0   | 121.0  |
| After thawing:                           |  |  |   |  |
| Weight of berries, grams.....            | 144.3  | 148.7  | 163.3   | 188.0  |
| Weight of sirup, grams.....              | 235.0  | 193.0  | 200.6   | 134.1  |
| Balling degree of sirup.....             | 30.5   | 47.45  | 32.3  | 48.9   |
| Calculated data:                         |  |  |   |  |
| Weight absorbed by container, grams..... | 5.2  | 5.8  | 5.0   | 5.0  |
| Weight lost by evaporation, grams.....   | 17.2   | 14.2   | 34.8  | 32.2   |
| Water withdrawn from berries, grams..... | 104.8  | 121.3  | 95.1  | 105.7  |
| Sugar absorbed,* grams.....              | 9.2  | 30.3   | 15.7  | 55.4   |
| Sugar absorbed,† grams.....              | 6.4  | 27.0   | 16.6  | 52.2   |
| Sugar absorbed, grams (average).....     | 7.8  | 28.6   | 16.15   | 53.8   |
| Per cent sugar absorbed.....             | 3.2  | 11.75  | 6.7   | 22.3   |

\* Weight of sugar added minus weight of sugar in drained sirup.

† Weight of water withdrawn from berries minus weight lost by berries.

A calculation of the amount of sugar absorbed by the sliced peaches, postulating the simple mechanism described in the introductory paragraph of this section, was made. It was found that a variable amount of water was withdrawn from the fruit, increasing with increase in concentration of sirup; and that a loss of sugar from the peach tissues occurred when concentrations of sirup of 40° Balling or less were used, but an absorption occurred in sirups of higher concentration.

An extended calculation of sugar absorption by Banner strawberries packed in sugar and in sirup and frozen in air at 0° F with and without preliminary storage at 32° F for 24 hours was made and a summary of the results obtained is given in table 17 to show the method of cal-

culation. The strawberries were packed in paraffin-impregnated tub-shaped paper containers and stored at 0° F for over a year. They were then removed from storage, allowed to thaw for a period of 16 hours, drained over a 1/8-inch mesh screen and the drained weight of fruit, the weight of sirup, and the concentration of the sirup determined. The

TABLE 18  
ABSORPTION OF SUGAR BY BANNER STRAWBERRIES  
(Calculated by "sugar-balance" method)

| Pack                     | Concentration of sirup, per cent | Ratio of fruit to sugar* | Loss in weight, per cent | Water withdrawn from berries, per cent | Sugar absorbed by berries, per cent† |
|--------------------------|----------------------------------|--------------------------|--------------------------|--|--------------------------------------|
| Cane-sugar sirup.....    | 10                               | .....                    | 37.4                     | 27.4                                   | - 6.2                                |
|                          | 20                               | .....                    | 34.1                     | 28.4                                   | - 3.7                                |
|                          | 30                               | .....                    | 27.5                     | 24.6                                   | - 0.9                                |
|                          | 40                               | .....                    | 29.1                     | 27.8                                   | 1.0                                  |
|                          | 50                               | .....                    | 26.5                     | 28.4                                   | 3.7                                  |
|                          | 60                               | .....                    | 31.7                     | 30.8                                   | 1.6                                  |
| Invert-sugar sirup‡..... | 10                               | .....                    | 34.3                     | 25.1                                   | - 5.7                                |
|                          | 20                               | .....                    | 31.3                     | 24.8                                   | - 3.1                                |
|                          | 30                               | .....                    | 30.2                     | 26.2                                   | - 1.3                                |
|                          | 40                               | .....                    | 29.3                     | 27.6                                   | 1.7                                  |
|                          | 50                               | .....                    | 27.8                     | 29.1                                   | 4.2                                  |
|                          | 60                               | .....                    | 28.8                     | 31.5                                   | 5.7                                  |
| Cane sugar.....          | .....                            | 1 : 1                    | 38.5                     | 44.3                                   | 8.5                                  |
|                          | .....                            | 2 : 1                    | 34.6                     | 40.5                                   | 7.5                                  |
|                          | .....                            | 3 : 1                    | 35.5                     | 37.8                                   | 3.8                                  |
|                          | .....                            | 4 : 1                    | 38.0                     | 38.2                                   | 1.7                                  |
|                          | .....                            | 5 : 1                    | 34.7                     | 36.5                                   | 3.3                                  |
|                          | .....                            | 6 : 1                    | 38.7                     | 38.7                                   | 1.6                                  |
| Invert sugar‡.....       | .....                            | 1 : 1                    | 31.6                     | 38.9                                   | 10.1                                 |
|                          | .....                            | 2 : 1                    | 36.4                     | 40.6                                   | 6.2                                  |
|                          | .....                            | 3 : 1                    | 30.5                     | 35.4                                   | 6.5                                  |
|                          | .....                            | 4 : 1                    | 30.0                     | 34.3                                   | 5.7                                  |
|                          | .....                            | 5 : 1                    | 34.5                     | 36.6                                   | 3.9                                  |
|                          | .....                            | 6 : 1                    | 37.1                     | 37.5                                   | 2.0                                  |

\* The ratio of fruit to sirup was maintained at 1 1/2 : 1.

† Invert sugar tested 76.3° Balling.

‡ Minus sign indicates loss of sugar.

results presented in table 17 are averages of three determinations. An appreciable absorption of sirup by the containers took place, as they increased in weight about 5 grams. A loss of water by evaporation also occurred. It is seen that preliminary storage at 32° F before freezing practically doubled the absorption of sugar by the berries. Owing to losses due to absorption by the container and evaporation in storage which can be corrected for only approximately, the absorption of sugar calculated by a "sugar balance" did not agree exactly with that calculated by a "water balance."



The results of a more extensive investigation on the absorption of sugar by Banner strawberries as calculated by the "sugar balance" method is shown in table 18. The results shown are averages of three determinations. It is seen that both in the cane-sugar and invert-sugar sirups a loss in sugar from the berries apparently occurred in sirups of concentrations up to 40 per cent sugar; but an absorption of sugar occurred at higher concentrations. The absorption of sugar was greater in the invert-sugar sirup packs than in cane-sugar sirup and a more regular increase of sugar absorbed with increase in concentration of sirup occurred. Similar results were found with berries packed in sugar; the amount of sugar absorbed decreased with increase in the ratio of fruit to sugar, was greater than that found in sirup packs, and the trend was more regular in invert-sugar series than in cane-sugar series.

There was more variation in sugar absorbed than in water withdrawn. The water withdrawn increased somewhat, but not markedly and not regularly with increase in concentration of sugar or sirup. The loss in weight found was not equal to that calculated from the difference between water withdrawn and sugar absorbed, although it was of the same order of magnitude. This may be due to certain inaccuracies in results such as failing to completely correct for evaporation and carton absorption losses, or to errors in the postulated mechanisms. The latter is probably the case.

Diehl *et al.*<sup>(3)</sup> report that "determinations of soluble solids made on the juice taken from the center portions of the berries packed in different cane sugar concentrations, as well as that pressed from the outer portions of the fruit do not show consistent differences such as would occur if there were an actual penetration of sugar into the fruit tissue." However, in a later personal communication, Diehl reported that sugar penetration was found to take place.

### OXIDATION CHANGES AND THEIR CONTROL

*Discoloration of Fruits.*—In the presence of air, darkening of the tissues, deterioration of color and development of unnatural flavors occur in certain fruits, even at freezing temperatures, owing to the oxidation of certain constituents. This oxidation is due in great part to the activity of the oxidases present in the fruit tissues. Although the fresh fruit is resistant to oxidation, the injury to the tissues by freezing allows mixing of the cell contents with consequent rapid oxidation upon exposure to air. As a result, although oxidation occurs during freezing storage, it

is more profound upon thawing. Changes in color in the presence of air during freezing storage occur at a reduced rate but become apparent in the course of two to six months.

All varieties of fruit were not found to be equally subject to marked deterioration of color and flavor by oxidation. Figs, red grapes, black cherries, plums, persimmons, and melons are practically free from oxidative deterioration during a period of storage of six to eight months. Berries suffer more in flavor than in color. Apples, apricots, avocados, peaches, pears, light-colored cherries, plums, and grapes, are subject to marked deterioration in color and flavor when frozen in air. These fruits apparently contain active oxidases.

Discoloration of frozen fruit by oxidation can be prevented<sup>(2, 6, 11)</sup> by (a) destroying the enzyme by heat; (b) by excluding air by packing under vacuum or submerging in sirup; (c) by the use of sulfurous acid; and (d) by the use of strong acids. It was found that the heating necessary to destroy oxidases also adversely affected the flavor of the fruit; and that although exclusion of air by packing fruits in sirup under vacuum or in hermetically sealed containers actually protected the fruit during storage and thawing in the sealed can, oxidation occurred when the fruit was exposed to air during consumption. Discoloration can also be minimized by selection of suitable varieties of fruits, as pointed out by Diehl.<sup>(4)</sup>

To determine the severity of sulfur dioxide treatment necessary to preserve the color of Gravenstein apples, Blenheim apricots, and Elberta peaches, the sliced fruits were dipped for 1, 5, 10, 30, and 60 minutes, in sulfurous acid solutions containing 500, 1,000, 1,500, and 2,000 p.p.m. of sulfur dioxide; the samples were then drained and frozen in petri dishes. After 20 hours at 0° F the samples were removed and exposed at room temperature. After 24 hours, it was found that treatment for 1 minute in 500 p.p.m. of sulfur dioxide solution was sufficient to preserve the color of peaches and apricots; but 10 minutes was necessary for apples. In another test Blenheim apricots and Elberta peaches were packed in a sirup of 40 per cent sugar containing 200 p.p.m. of sulfur dioxide and in sirup of 40 per cent sugar after being held for 5 minutes in a solution of 500 p.p.m. sulfur dioxide. Both treatments were found to preserve the color upon exposure to air during thawing, for over 24 hours. Packing in sirup containing a small amount of sulfur dioxide was found preferable, since the flavor of the product was better. To determine the minimum concentration of sulfur dioxide in the sirup necessary to preserve color, sliced Phillips Cling peaches were packed in hermetically sealed containers in sirup containing 50,

100, 200, and 500 p.p.m. of sulfur dioxide. Sirup containing 100 p.p.m. of sulfur dioxide preserved the color and flavor without adversely affecting the flavor; but in sirup containing more than this amount of sulfur dioxide, the preservative was detectable by taste.

In order to determine the effect of method of lye peeling and of rinsing in acid, Phillips Cling peaches were lye-peeled by immersion in 2½ per cent NaOH at 212° F for ½ minute and by immersion in 10 per cent lye at 140° F for 2 minutes. The peeled fruit was washed in water and then frozen in sirup of 40 per cent sugar content with and without rinsing in either 2 per cent citric acid solution or 2 per cent hydrochloric acid solution. Both lye-peeling methods not accompanied by rinsing in acid resulted in marked surface discoloration of exposed peaches. Rinsing in 2 per cent hydrochloric acid resulted in fruit that was too sour in flavor, while a 2 per cent citric acid did not check the surface darkening. Rinsing lye-peeled Elberta peaches in 3 per cent citric acid was found satisfactory. No difference such as described by Woodroof<sup>(13)</sup> for Elberta peaches was found between the two lye-peeling methods applied to Phillips Cling peaches.

In the course of our studies on temperature changes in foods in 1930 we found that whole peaches frozen in solid carbon dioxide darkened more rapidly and pronouncedly than did those frozen in air at 0° F both during freezing storage and thawing. A comparison between certain clingstone and freestone varieties of yellow-fleshed California peaches was made and in some cases it was found that clingstone varieties discolored more than the freestone. Apricots, apples, pears, peaches, and grapes in general were found to discolor more when immature than when mature. This is in accordance with reported experiments of oxidase activity in fruits in which it was found that the oxidase activity decreases with maturity.

Caldwell, Lutz, and Moon<sup>(2, 11)</sup> have reported that the discoloration of peaches of all varieties was most rapid and pronounced in immature fruits and decreased in intensity with advancing ripeness. They found the best stage of maturity for freezing purposes to be one day before full eating ripeness. They found no chemical treatment wholly effective in preventing discoloration and that although exposure to the fumes of burning sulfur or the addition of sodium bisulfite to the sirup completely prevented discoloration, the odor and taste of sulfur dioxide were distinctly evident. Sliced peaches frozen in solid carbon dioxide thawed more quickly than those frozen at 16° to 18° F in air. In hermetically sealed containers the quick-frozen and the slow-frozen fruit was in most varieties indistinguishable from the fresh in appearance, texture, and

flavor; but in a few varieties the quick-frozen fruit was slightly darker than the slow-frozen. In paper containers opened while still frozen, the quick-frozen material was in all varieties distinctly darker in color than slow-frozen, and this difference became more pronounced during defrosting. The degree of discoloration and the general quality of the product varied markedly with variety. White-fleshed varieties were found very unpromising and yellow-fleshed varieties differed widely. J. H. Hale, Reeves, Chairs, St. John, and Up-to-Date were found distinctly superior to the other varieties.

*Flavor Changes in Vegetables.*—Oxidative changes in vegetables result in the development of an unnatural haylike flavor rather than discoloration. Preliminary scalding or blanching of the vegetables followed by rapid chilling prior to freezing not only destroys the enzymes responsible for this change, but also improves the color of the product. Blanched vegetables are greener in appearance and the brine in which they are frozen is more nearly free from sediment.

In preliminary investigations<sup>(5, 6)</sup> it was found that blanching for about 2 minutes in steam or in boiling water, in brine, or in citric acid solution was sufficient to prevent the appearance of these haylike flavors during storage at 0° to 5° F for over eight months. Subsequently J. Barker<sup>(1)</sup> reported that partial cooking for 8 minutes prior to freezing in water prevented autolytic changes in peas during storage for over four months at 0° F. In order to determine the effect of the length of blanching and to compare blanching in steam and in water, early green peas of good quality in quantities of about 550 grams were blanched for varying lengths of time in steam and in boiling water. Accurately weighed amounts of blanched peas were placed with accurately measured volumes of brine containing 2 per cent salt (sp. gr. 1.014) in one-pound paraffin-impregnated paper tubs and the samples were then frozen in air at 0° F and stored for four weeks. They were then allowed to thaw completely and the drained weight, volume, and specific gravity of brine were determined.

The results are shown in table 19. It is evident that all of the samples blanched for a minute or longer either in steam or water gained in weight during freezing and subsequent thawing. It would seem from the data that it is impossible for the peas to absorb more than a certain maximum percentage of moisture. This maximum is greater in the steam-blanched peas than in water-blanched. A loss in the volume of brine occurs in the steam-blanched peas which increases rapidly with length of blanch but reaches a fairly constant amount after 3 minutes' blanching. Similar results were found for peas blanched in water. All



of the blanched samples were practically identical in texture, but somewhat more tender than the unblanched. The quality of the samples was determined after boiling the thawed vegetables in their own brine to which 200 cc of water was added. The cooking period was such that the time of blanching plus that of cooking was 12 minutes. In the opinion of 7 out of 9 persons who judged the cooked peas, those blanched in steam for 30 seconds and one minute were "good." The samples blanched in water for 3 minutes or less were judged as being "very good." A blanch

TABLE 19  
EFFECT OF BLANCHING ON CHANGE IN WEIGHT OF PEAS AND BRINE DURING FREEZING AND THAWING

| Treatment       | Before freezing       |                     | After thawing         |                     |                           | Percentage gain or loss in weight of peas | Percentage gain or loss in volume of brine |
|-----------------|-----------------------|---------------------|-----------------------|---------------------|---------------------------|---|--|
|                 | Weight of peas, grams | Volume of brine, cc | Weight of peas, grams | Volume of brine, cc | Specific gravity of brine |   |  |
| No blanch.....  | 237.5                 | 150                 | 211.0                 | 163.0               | 1.0240                    | -10.9                                     | + 8.7                                      |
| Steam blanch:   |                       |                     |                       |                     |                           |   |  |
| 30 seconds..... | 250.0                 | 140                 | 247.8                 | 130.5               | 1.0240                    | - 0.9                                     | - 7.0                                      |
| 1 minute.....   | 250.0                 | 140                 | 257.0                 | 126.0               | 1.0245                    | + 3.2                                     | -14.3                                      |
| 3 minutes.....  | 260.0                 | 150                 | 285.0                 | 116.0               | 1.0235                    | + 9.6                                     | -22.6                                      |
| 5 minutes.....  | 245.0                 | 150                 | 267.5                 | 116.0               | 1.0220                    | + 9.2                                     | -22.6                                      |
| 7 minutes.....  | 260.0                 | 150                 | 291.5                 | 112.0               | 1.0225                    | +12.1                                     | -25.3                                      |
| 10 minutes..... | 270.0                 | 150                 | 298.8                 | 115.0               | 1.0220                    | +10.4                                     | -23.4                                      |
| Water blanch:   |                       |                     |                       |                     |                           |   |  |
| 30 seconds..... | 250.0                 | 150                 | 257.0                 | 136.0               | 1.0240                    | + 2.8                                     | - 9.7                                      |
| 1 minute.....   | 260.0                 | 150                 | 277.3                 | 125.5               | 1.0230                    | + 6.7                                     | -14.6                                      |
| 3 minutes.....  | 270.0                 | 150                 | 289.3                 | 122.0               | 1.0215                    | + 7.1                                     | -18.6                                      |
| 5 minutes.....  | 250.0                 | 150                 | 270.7                 | 119.0               | 1.0195                    | + 8.3                                     | -20.6                                      |
| 7 minutes.....  | 240.0                 | 140                 | 257.0                 | 113.5               | 1.0180                    | + 7.0                                     | -22.7                                      |
| 10 minutes..... | 260.0                 | 150                 | 284.5                 | 115.0               | 1.0180                    | + 9.4                                     | -23.7                                      |

of over 3 minutes either in steam or boiling water was detrimental to the quality of the product. Prolonged blanching resulted in a decided leaching of soluble solids into the water bath and into the brine of those samples which were steam-blanched. Similar results were found with string beans. Subsequent investigations indicated that blanching for 60 seconds in steam retained the flavor of peas, string beans, and asparagus during freezing storage for more than a year.

#### CHANGES IN FLAVOR OWING TO CAUSES OTHER THAN OXIDATION

Some fruits and vegetables acquire during freezing and subsequent thawing a peculiar flavor and an odor which are sometimes undesirable and offensive. Weakly flavored fruits such as cling peaches apparently lose all of their characteristic flavor upon prolonged storage, even when

protected from oxidation. Grapes, apples, berries, and cherries sometimes acquire a rather undesirable flavor which seems to be more apparent in hermetically sealed containers in which they have not been promptly cooled and frozen. It is thought that this may be due to anaerobic respiration which occurs in the closed containers during freezing. Peaches also on long storage acquire a pronounced benzaldehyde flavor. This is more marked in freestones than in clingstones, and is more marked in exposed peaches although it occurs in those submerged in sirup. Sometimes off flavors are found as a result of the permeability of the paper containers allowing absorption of foreign cold storage odors and flavors, and often off flavors can be traced to absorption of foreign flavors from containers. These are more pronounced upon long storage. It was found that sliced pineapple, which was fair to good in flavor after three or four months' storage, suffered a complete loss in pineapple flavor and became markedly darkened after storage for ten months. This darkening and loss in flavor, however, may be due to oxidation since it was more pronounced in exposed slices of pineapple. Pineapple juice was decidedly not equal to the fresh after prolonged storage, but nevertheless had more pineapple flavor than the frozen fruit.

#### SUMMARY AND CONCLUSIONS

Observations made during the course of three years' study of a number of the physical and chemical changes occurring during the freezing storage and thawing of fruits and vegetables are reported here as a survey of the field. It is believed that a knowledge of these changes, of the conditions affecting them, and of the agencies causing them will lead to a development of more suitable methods of pretreatment, packing, freezing, and storing these products.

The chief factors that determined the rate of temperature change were the specific heat and heat conductivity of the product, the temperature at which ice began to separate, the amount of ice that separated under the freezing conditions, the size and shape of the container, the initial temperature, and the temperature of the refrigerant. The effect of neighboring containers in the case was more marked than the effect of types of cases studied.

The amount of expansion in volume on freezing decreased with increase in concentration of sugar or soluble solids. Expansion in whole fruit was less than in crushed fruit. Upon thawing, a decrease in original volume occurred.



The loss in weight of fruit upon thawing was a function of ice formation and osmotic action and depended upon the type and condition of fruit, the concentration of sugar in the sirup, the proportion of sugar and of sirup used, the kind of sugar, and the rate of freezing. The variation of loss in weight with concentration of sirup was found to be irregular.

Blanched vegetables as a rule increased in weight upon thawing if frozen with brine. The increase in weight increased with increase in the rate of freezing. Unblanched as well as blanched vegetables packed without brine decreased in weight.

No direct relation between change in texture and loss in weight was found, but in general the greater the loss in weight, the more severe was the change in texture.

There was but little loss in pectin by hydrolysis by naturally occurring enzymes in berries, but an appreciable inversion of sucrose was found. This was confirmed in investigations with pure invertase.

Increase in the concentration of soluble solids in fruit frozen with sugar or sirup was due to penetration of sugar into the fruit as well as withdrawal of water by the osmotic action of the added sugar.

Fruit exposed to air during freezing or during or after thawing will darken and discolor and develop unnatural flavors if active oxidases are present. It was impossible to inactivate the oxidases by heat without destroying the delicate fruit flavors, and permanent inhibition of oxidase by means of acid or reducing agents such as sulfur dioxide affected the flavor of the fruit adversely to some degree.

Oxidative changes in vegetables resulted in the development of unnatural haylike flavors. It was found that the development of these flavors could be inhibited and the flavor and color of the vegetable improved by blanching in steam or boiling water.

Changes in flavor owing to changes other than oxidation also occurred on prolonged storage. The development of benzaldehyde flavor in peaches and cherries and of off flavors, probably due to anaerobic respiration, were especially noticeable.

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